THE LEACHING OF ORGANOTIN COMPOUNDS FROM PVC PIPE

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THE LEACHING OF ORGANOTIN COMPOUNDS

FROM PVC PIPE

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SUMMARY

The migraion of organotin stabilizers from 3/4 in., Sch. 80 polyvinyl chloride pipe into ultra high purity double-deionized water (HPDDW) flowing through the pipe was examined as a function of time and flow rate. A recirculation system, which included 150 feet of PVC pipe being tested, was charged with 20 gallons of HPDDW. Reynolds numbers of 29,680, 14,840 and 7,420 were examined. The leaching rate was found to be a decaying exponential function which decreased significantly during a period of four hours with recirculation. The leaching results from stabilizer at or near the inner wall of the pipe. Diffusion of stabilizer from the bulk of the pipe wall to the inner wall was apparently negligible. In the test system, an equilibrium was attained between the inner wall of the PVC pipe and the HPDDW.

Based on results of dynamic tests on unleached pipe, the mass transfer coefficient was determined to be proportional to the Reynolds number raised to the 0.62 power. Considering the scatter in the data, the value of 0.62 agrees favorably with the value of 0.80 reported by Sieder and Tate.

Scanning electron microscopy was used to examine 44 samples of the inner surface of PVC pipes. Since the surface varied considerably in its features, no definite pattern

of change in the surfaces due to leaching was observed. However, the surfaces of leached samples were apparently somewhat smoother than the surfaces of unleached samples.

CHAPTER I

INTRODUCTION

Of all plastics known, polyvinyl chloride (PVC) and its compositions probably has the largest volume production on a worldwide basis. Since PVC is not naturally stable in commercial use, its acceptance on such a large scale is due principally to the incorporation of various stabilizers into the PVC resin. One of the major classes of stablizers is the organotin compounds.

The use of stabilizers in PVC results in improved resistance to light induced deterioration and, more importantly, improved resistance to heat induced deterioration (14). The disadvantage of using organotin compounds which prompted this study is their toxicity (15, 18). A major use of PVC is in the manufacture of pipe. Persons who use PVC pipe for conveying potable water might be exposed to undue risk if significant leaching of the stablizer from the pipe to the water supply takes place.

Recent experimental testing by National Sanitation Foundation (19) showed that leaching of organotin stablizer took place when pipes were contacted with water under static conditions. In these tests, ten out of ten samples of PVC pipe failed to meet a 0.05 ppm standard for tin. While

0.05 ppm may not seem to be a very high level, a recent report describing chronic, low-level studies concluded a dose of dibutyltin sulfide in an amount of 0.1 mg/kg (100ppb) has an effect. This study also recommended a maximum safe level of 20 ppb of the organometallic agents (11).

The assessment of potential hazards which might result from the leaching of organotin stablizer from PVC pipe would seem to be most profitably accomplished using a system which simulates actual conditions of use. For this reason, a pipe loop testing system in which dynamic tests could be run under controllable conditions was assembled. The primary aim was to determine mass transfer coefficients and leaching rates as a function of flow rate and time.

In addition to the dynamic tests, scanning electron microscopy was also implemented in an effort to determine the mechanism by which organotin compounds leach from PVC pipe to the water supply. Microscopy was used to examine the inner surfaces of sections of leached and unleached pipe.

CHAPTER II

GENERAL DISCUSSION AND LITERATURE REVIEW

The effect of fluid physical properties on the rate of convective mass and heat transfer to Newtonian fluids flowing turbulently inside tubes has been studied extensively. The equations of Chilton and Colburn (12), Sieder and Tate (17), and Harriot and Hamilton (9) all have the following form:

$$Nu = c_1(Re)^{c_2}(Sc)^{c_3} \tag{1}$$

Nu, Re, and Sc are the Nusselt, Reynolds, and Schmidt numbers, respectively. Significant differences in the numerical values of c_1, c_2, and c_3 have been reported. The discrepancies indicate that the use of such correlations are limited to certain ranges of Reynolds numbers and Schmidt numbers.

Friend and Metzner (7) developed an equation for heat and mass transfer that provided reasonable agreement with experimental data for smooth pipe with Schmidt numbers greater than 0.7. Their semitheoretical correlation

$$Nu = \frac{ReSc(f/2)}{1.20 + 11.8\sqrt{f/2}\,(Sc-1)Sc^{-1/3}} \tag{2}$$

is not applicable to systems such as liquid metals in which

most the resistance to transfer is in the turbulent core. Hughmark (10) took the resistance in the turbulent core into account and presented a three-resistance model:

$$\frac{1}{k^+} = \frac{1}{\frac{0.675}{Sc} + 0.062\ Sc^{-2/3}} + \frac{1}{\frac{1}{33Sc} + 0.0615\ Sc^{-1/2}} + \frac{1}{\frac{3.58\ D_A}{Ru^*} + 2\sqrt{f/2}} \tag{3}$$

Using the relationship given by Bird (2), et. al. results in:

$$Nu = ReSc\sqrt{f/2}\ k^+ \tag{4}$$

The applicability of these correlations to our system may be somewhat limited since they were developed for homogeneous mass transfer from wall solution data (9) or electrochemical data (12).

Berens and Daniels (1) have developed a predictive model for the migration of vinyl chloride monomer (VCM) from rigid PVC pipe. They combined the solubility and diffusion data obtained for VCM in uncompounded PVC resin powders with the Fickean diffusion equation. The considered the case of a freshly extruded PVC product, quickly cooled to ambient temperature and stored in a VCM free atmosphere. The initial VCM concentration in the product was uniform. At the surface, equilibrium was quickly established with the environment and the VCM concentration was zero. Due to sufficient air

circulation, the surface concentration remained zero. Crank (4) gives the solution of this problem for a hollow cylinder; however, the predictions for hollow cylinders are virtually identical to those for plane sheets, providing the wall thickness is less than the inside diameter. Equations for the amount of VCM escaping from the sheet was expressed in terms of the fraction of original VCM, M, which escapes.

Similarly, with pure water flowing through the pipe, the surface concentration of the organotin stabilizers might be essentially zero. With low levels of migration, the concentration of stabilizers in the dynamic test water would be essentially zero. The Berens and Daniels model is for migration from both surfaces of the sheet; but, in our case, only the inner surface is leached. Therefore, a possible model for our case might be:

$$M = 2\left(\frac{D_A}{\pi L^2}\right)^{1/2} t^{1/2} \qquad (5)$$

D_A is the diffusion coefficient of the stabilizer in PVC, L is the pipe thickness, and t is time. This equation is valid until the organotin stabilizer concentration at the midline of the pipe wall falls below its initial value.

The organotin stabilizers which have achieved widespread commercial success are derivatives of butyltin, methyltin, and octyltin. Usually a mixture of the mono- and dialkyl derivatives is employed. Trialkyltin contents are

from the film to water was obtained.

Hansen (8) in his study of solvent evaporation from a polymer film concluded that the initial stage in which the surface is wet with solvent is controlled by boundary layer phenomena, and that in the final stage, solvent evaporation is controlled by internal diffusion. The idea of two stages of migration may prove useful in the leaching of organotin stabilizers from PVC pipe, such that the initial stage is controlled by a mass transfer coefficient and the final stage is controlled by internal diffusion.

CHAPTER III

EQUIPMENT AND INSTRUMENTATION

Dynamic Test System

Due to the low leaching rate of the organotin stabilizer from the pipe to the water, a large contact time in the dynamic test system was required. Therefore, a recirculation system was constructed consisting of a surge tank, pump, orifice meter, various inert fittings, and 150 feet of PVC pipe, as shown in Figure 1. The major concern in the selection of materials for equipment other than the pipe was that they would not contriubte tin or remove tin from the system.

The materials studies indicated that 304 stainless steel, polyethylene, and polypropylene were acceptable materials. The materials studies are discussed further in Appendix B.

A 105 gallon cylindrical polyethylene tank and cover were obtained from the United Stated Plastic Corp. (Lima, Ohio). It was used as the surge tank. The tank is 36 in. diameter and 24 in. height.

The outlet of the tank, as indicated by Figure 1, leads to a March Mfg. Co. (Glenview, Ill.) Model TE-7R MD magnetically coupled pump. A magnetically coupled pump was

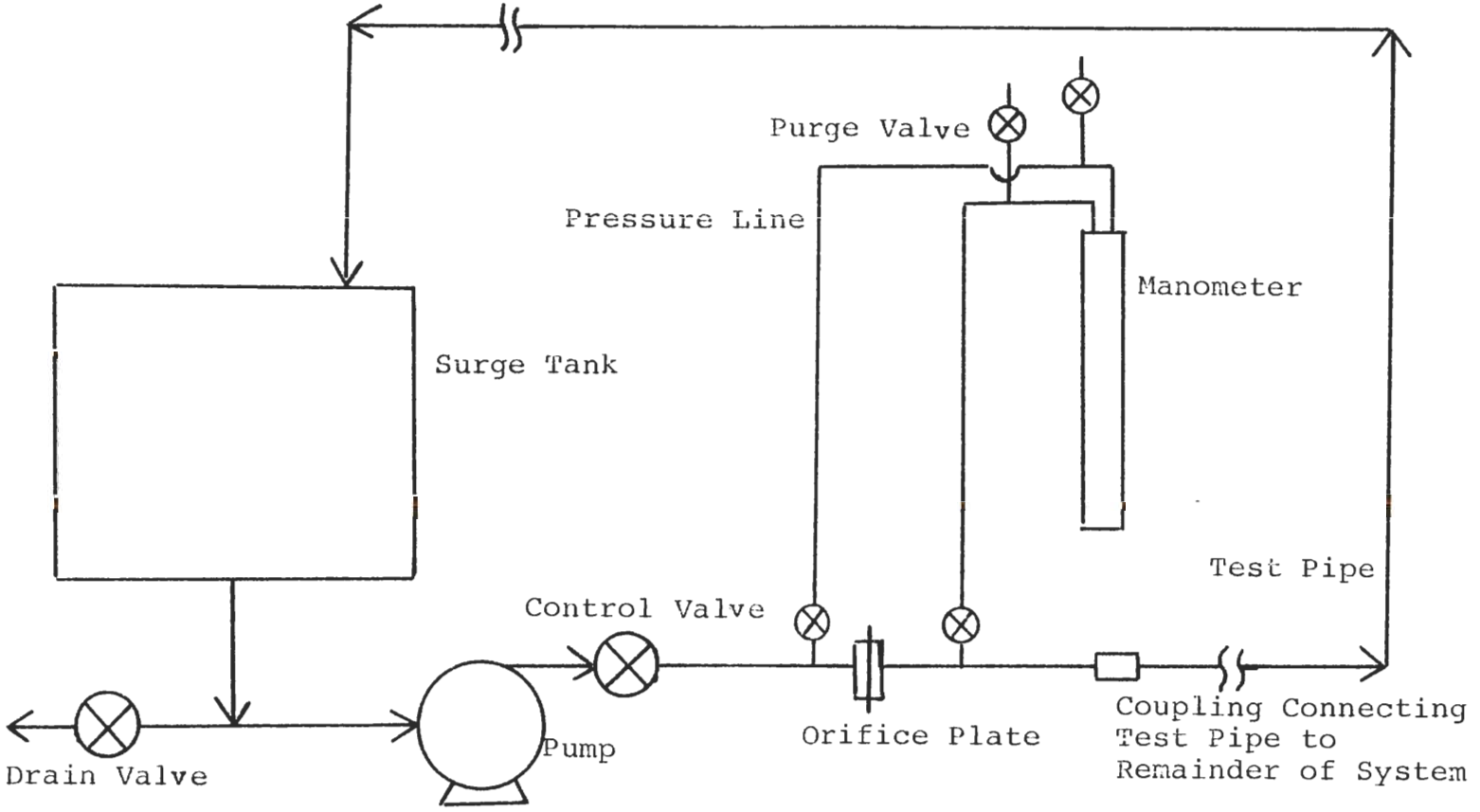


Figure 1. Schematic of Dynamic Pipe Loop System.

used in order to avoid seepage of test water through a stuffing box or contamination with oil from a mechanical seal. Next on line is a one inch 304 stainless steel globe valve used to regulate the flow rate through the pipe loop system.

Following the control valve is a one inch orifice meter constructed in the machine shop at Georgia Tech. The pressure taps on the orifice meter were connected with a 40 in. water over oil U-tube manometer. The oil, Merian 175 Blue Fluid, has a specific gravity of 1.75. Valves which vented to the atmosphere were connected to the pressure lines so that air and possibly contaminated water could be purged from the lines. Valves were also placed at the pressure tap-pressure line junctions in order to isolate the manometer from the rest of the system when flow rate was not being measured; hence, the possibility of contamination of test water by manometer fluid was minimal. The orifice meter was calibrated for pressure drop versus flow rate of water through the meter.

The orifice meter leads to the 150 feet of PVC pipe being tested and various elbows, couplings and unions needed to connect the sections of pipe. The PVC pipe is mounted with a one degree upward gradient to prevent air entrapment. The PVC pipe leads directly back to the surge tank.

The water used in the pipe tests was processed by a Continential Water Conditioning unit. The manufacturer's

specifications indicate that the processed water had a tin concentration less than 0.1 ppb. Tests run in the EES laboratories confirmed that the system was operating within specifications.

Analytical Method

The chemical analyses were conducted by various members of the staff at the Georgia Tech Engineering Experiment Station. Since the experimental organotin concentrations were of the order of several ppb of tin, the development of an accurate technique for the quantitative analysis of organotin in water samples from the dynamic tests and materials studies was a difficult task. Some success was achieved with anodic stripping voltametry. The instrument used was a PAR Model (Princeton, N. J.) Model 174 A Polarographic Analyzer. This technique was used for the materials studies and some of the earlier pipe loop samples. However, the voltametry did not yield results which were as reproducible as desired. Other quantitative analysis techniques were considered.

The flameless atomic absorption (AA) technique proved to be the most reproducible of the methods tested. The advantages of AA over voltametry included the following:

1. Smaller sample aliquots were needed to run an analysis.
2. Less time was needed to run an analysis.
3. Less handling was needed to prepare a sample for analysis.

The instrument used was a Perkins-Elmer (Norwalk, Conn.) Model 303 Atomic Absorption Spectrophotometer equipped with a Model HGA-2100 heated graphite furnace. The AA technique was used to analyze all reported dynamic pipe loop samples. The AA technique will be discussed further in Appendix C.

Electron Microscopy

The instrument used for the scanning electron microscopy was the JEOL (Medford, Mass.) 100C-AS10-ASD-YDID. To prevent static charge build up on the samples examined, a gold and palladium coating was applied to the samples using an International Scientific Instrument (Palo Alto, Calif.) Model PS-2 Coating Unit.

CHAPTER IV

PROCEDURE

Pipe Loop Test Procedure

The dynamic test system was set up in such a way that the tank, pump, valves, and orifice meter needed only to be assembled once. The pipe choosen to be tested was 3/4 in., Sch. 80 Harvel PVC 1120, Code 77-G-17-OCT. It was obtained in standard 20 ft. sections. Three samples of Harvel PVC pipe were found to contain 400 ($\pm$60) ppm tin by neutron activation analyses (20). For each test, 150 feet of PVC pipe was set up on pipe stands. The pipe was cut where necessary and threaded. Although most PVC pipe is connected with glued fittings, the chance of interference from the glue was deemed undesirable. The pipe was connected with the following threaded fittings: seven elbows, five couplings, one tee, and one union. Teflon tape was used at the threaded joints to prevent leakage of test water out of the system.

In order to remove shavings of PVC pipe resulting from threading, pieces of teflon tape, and other debris, the system was rinsed after completion of set up. The control valve and drain valve were closed and the tank was filled with approximately 20 gallon of water processed by the Continental Water System. Approximately eight gallon of the water was pumped

through the test pipe but not allowed to return to the tank. This rinse water and the remainder of the water in the tank was then discarded.

After the tank was drained, 20 gal. of test water, also processed by the Continental Water System, was placed in the tank and the test was begun. Timing of the experiment began when the pump was started and the control valve was opened. The desired flow rate was quickly established in each run. The valves at the pressure tape on the orifice meter were opened. Air was purged from the pressure lines by opening up a second set of valves located at the high point in pressure lines, which vent to the atmosphere. After the air was purged, the air vents on the lines were closed. The control valve was then adjusted to obtain the pressure drop reading corresponding to the proper flow rate. After the flow rate had been set, the valves at the pressure taps were also closed to avoid a chance of interference from the manometer oil. The three flow rates studied were 6.074, 3.037, and 1.519 gallons per minute.

Samples were taken at various times by collecting approximately 50 ml. of the test water returning to the tank. The samples were placed in snap cap plastic vials. Nine ml. of test water and one ml. of high-purity 6N hydrochloric acid, HCl, were pipetted into each sample vial. The HCl was added to preserve the sample and to prepare it for quantitative analysis of organotin compounds.

The method of analysis was flameless atomic absorption spectroscopy. The method of analysis is discussed in Appendix C.

In addition to testing previously unleached pipe, two tests using leached pipe were also made. For each test, processed water was first recirculated at 6.074 GPM through 150 feet of unleached test pipe. The periods of recirculation were 10.33 days and 13.06 days for Test No. 1 and Test No. 2, respectively. The system was then drained. Before beginning a test on the previously leached pipe, the system was rinsed three times by filling the tank with 20 gallons of processed water. Then the water was circulated through the pipe loop for approximately three minutes before draining. After completion of the rinsing, the tank was filled with 20 gallons of processed water to be used in the test. As in the other dynamic tests, recirculation was begun and the flow rate was then set. In Test No. 2, the flow rate was set at 3.037 GPM. In Test No. 1, the flow rate was set at 6.074 GPM; then, after 12.41 days, the flow rate was reset at 3.037 GPM, and then, after 18.83 days at 3.037 GPM, the flow rate was again reset at 6.074 GPM. Samples were collected in the same manner as described previously.

The ambient temperature and atmospheric pressure remained approximately constant at 21°C and 740 mmHg, respectively, during all pipe loop tests. In the dynamic pipe loop tests, the temperature of the test water was

approximately 5°C above the ambient temperature due to the energy input of the pump.

In addition to the dynamic pipe loop tests, a static pipe loop test was made with 4.97 meters of test pipe. Using two elbows, a U-shaped pipe loop was set up. The base of the U-shaped loop was 0.71 meters and each arm was 1.88 meters. The loop was rinsed for approximately one minute, and then filled with processed water at time zero. The samples were withdrawn with a syringe and four feet of tubing. The arms of the U-shaped loop pointed upward; therefore, as the test water was withdrawn, the ratio between inner surface of the test pipe in contact with the test water and the volume of the test water remained approximately constant.

Scanning Electron Microscopy Procedure

The inner surfaces of PVC pipe examined by scanning electron microscopy (SEM) were prepared in several ways. Most of the samples of pipe examined were the same type of pipe tested in the dynamic pipe loop tests, 3/4 in., Sch. 80 Harvel PVC 1120 pipe. Some of the pipe samples were leached statically by submerging sections in high-purity water, sealed in a polyethylene bottle. Some of the samples were stored at slightly elevated temperatures in order to accelerate changes in the surface due to leaching. A control sample, sealed in a bottle containing no water, was stored in the same manner as the samples which were leached.

Some of the SEM samples were leached by submerging

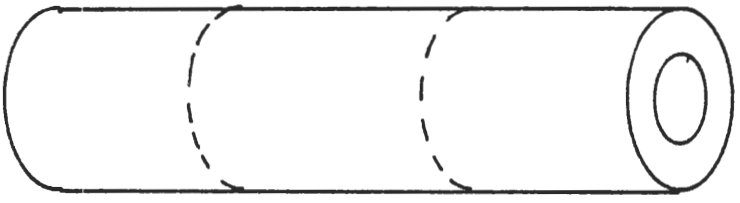
12 centimeters sections of pipe in a water filled beaker. At the end of the leaching period, the sections of pipe were removed from the water and the inner pipe surface was prepared from SEM. A sample size suitable for mounting was limited to approximately 20 mm in length, five mm in width, and one mm in depth. The procedure for sizing a pipe section for SEM, illustrated schematically in Figure 2, is as follows:

1. A section of pipe was cut to the length of the mounted sample.
2. A portion of the outside wall of this section was ground to a depth no more than one millimeter from the inner wall.
3. The ground portion was then cut out with two parallel cuts, no more than five mm apart, along the length of the section.

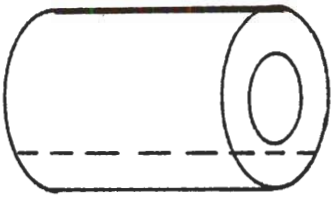
Some samples were first sized for mounting, and then leached or used as a control.

In order to prevent the build up of static charge on the sample during examination with SEM, an electrically conducting coating was placed on the surface of the sample prior to examination. Initially, a graphite coating was used to establish electrical conductivity; however, the graphite coating failed in some cases. A gold and palladium coating for the SEM samples was found to be satisfactory and was used on all but a few initial SEM samples.

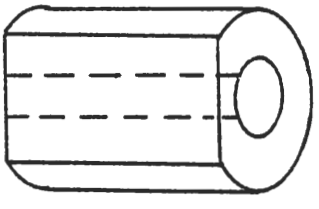
In addition, a gold and palladium coating was placed



A section of pipe was cut to the length of the mounted sample.



A portion of the outside wall of this section was ground to a depth no more than one millimeter from the inner wall.



The ground portion was then cut out with two parallel cuts, no more than five mm apart, along the length of the section.

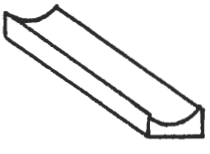


Figure 2. Steps in Preparing SEM Sample.

on a portion of some samples prior to submerging the sample in water. This initial coating was used to prevent changes in the coated surface.

CHAPTER V

RESULTS AND DISCUSSION OF RESULTS

Pipe Loop Tests

After examination of the calculated results from the dynamic pipe loop tests listed in Appendix E, several characteristics were obvious. In each test, the concentration of tin in the test water attained a constant value. Also, in the dynamic tests on unleached pipe, the rate of increase in the tin concentration decreased as the period of recirculation increased. In the tests on leached pipe, the concentration of tin in the water reached a value significantly lower than the concentration reached in the tests on unleached pipe.

Based on these characteristics in the experimental data, several assumptions were made. The assumptions were as follows:

1. The test water attained an equilibrium with the concentration of tin at or near the inner pipe wall.
2. The concentration of tin at or near the inner pipe wall was not replenished by tin from the bulk of the pipe wall.
3. In the water, at the pipe-water interface, a mass transfer coefficient was applicable.

With these assumptions, a theoretical model was developed. The development of the model is as follows:

$$N_A = -K_x(k_1 c_w - c)/MW_A \qquad (6)$$

where N_A = molar flux of tin from the inner pipe wall into the water flowing through the pipe

K_x = mass transfer coefficient

k_1 = equilibrium constant between c_w and c (i.e., $k_1 = (c/c_w)$ equilibrium)

c_w = concentration of tin at or near the inner pipe surface in terms of mass per unit area.

c = concentration of tin in the test water at time t in terms of mass per unit volume

MW_A = molecular weight of tin

Assuming the concentration of tin at or near the inner pipe wall is not replenished by the diffusion of organotin compounds from the bulk of the pipe wall the relationship for c_w and c is as follows

$$c_w = c_{wo} - k_2 c \qquad (7)$$

where c_{wo} = c_w at time zero

k_2 = constant which relates a change in c to a change in c_w

Since

$$N_A = \frac{1}{MW_A} \frac{dc_w}{dt} \tag{8}$$

then

$$N_A = \frac{1}{MW_A} \left(-k_2 \frac{dc}{dt}\right) \tag{9}$$

and

$$k_2 \frac{dc}{dt} = K_y(k_1 c_w - c) \tag{10}$$

Letting $k_3 = K_x/k_2$, Eq. 10 becomes

$$\frac{dc}{dt} = k_3(k_1 c_w - c) \tag{11}$$

Substituting in Eq. 7 and simplifying, Eq. 11 becomes

$$\frac{dc}{dt} = k_4 - k_5 c \tag{12}$$

where

$$k_4 = k_1 k_3 c_{wo}$$

$$k_5 = k_3(k_1 k_2 + 1)$$

Rearranging Eq. 12, it becomes

$$\int_o^c \frac{dc}{k_4 - k_5 c} = \int_o^t dt \tag{13}$$

Integration of Eq. 13, and letting $k_6 = k_4/k_5$ yields

$$\ln \left(\frac{k_6 - c}{k_6}\right) = -k_5 t \tag{14}$$

Exponentiation of both sides of Eq. 14 and rearrangement yields the model

$$c = k_6(1 - e^{-k_5 t}) \tag{15}$$

The values of k_6 and k_5 were determined by fitting the experimental data for a given pipe loop test with Eq. 15 using a least squares criteria. The optimum fit for each test was obtained using the computer subroutine PATERN (13), a numerical search for multidimensional optimization.

The results of the dynamic pipe loop tests of previously unleached pipe are indicated by Figures 3, 4, and 5. Along with the experimental results is the model fitted for the test results. The parameters of the model are given in Table 1. The results of the dynamic pipe loop tests on leached pipe are shown in Figure 6 and 7. The equilibrium concentration of tin in the test water attained in the tests on leached pipe are 1.22 ppb and 1.12 ppb for Test No. 1 and Test No. 2, respectively.

The maximum concentration, as indicated by the value of k_6, is approximately 5.9 ppb Sn. Since the system was charged with 20 gallons of water, the 5.9 ppb Sn indicates that 4.46×10^{-4} grams of tin was leached from the PVC pipe.

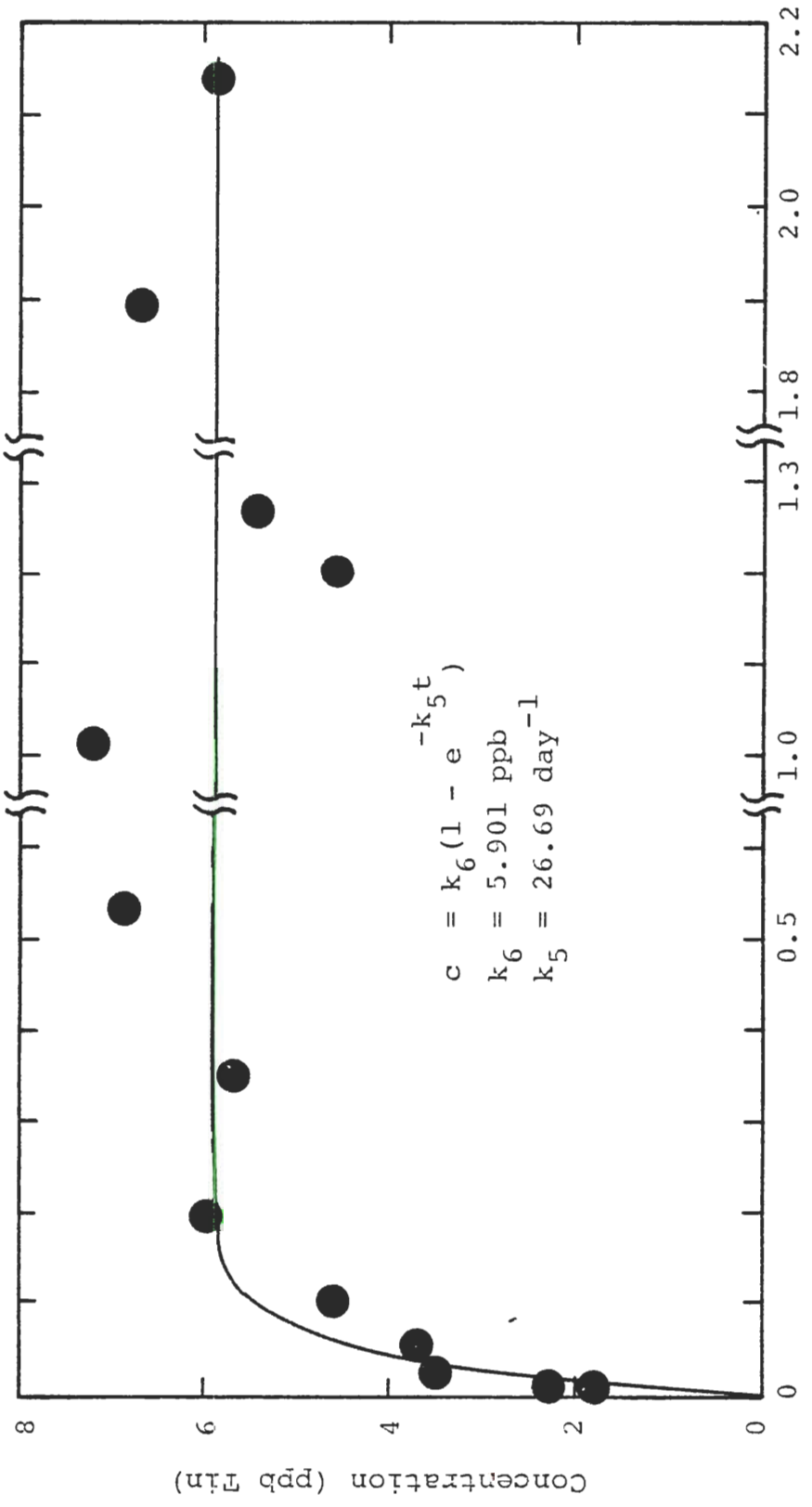


Figure 3. Experimental Results Shown on Concentration of Tin Plotted Against Time for 6.074 GPM Test.

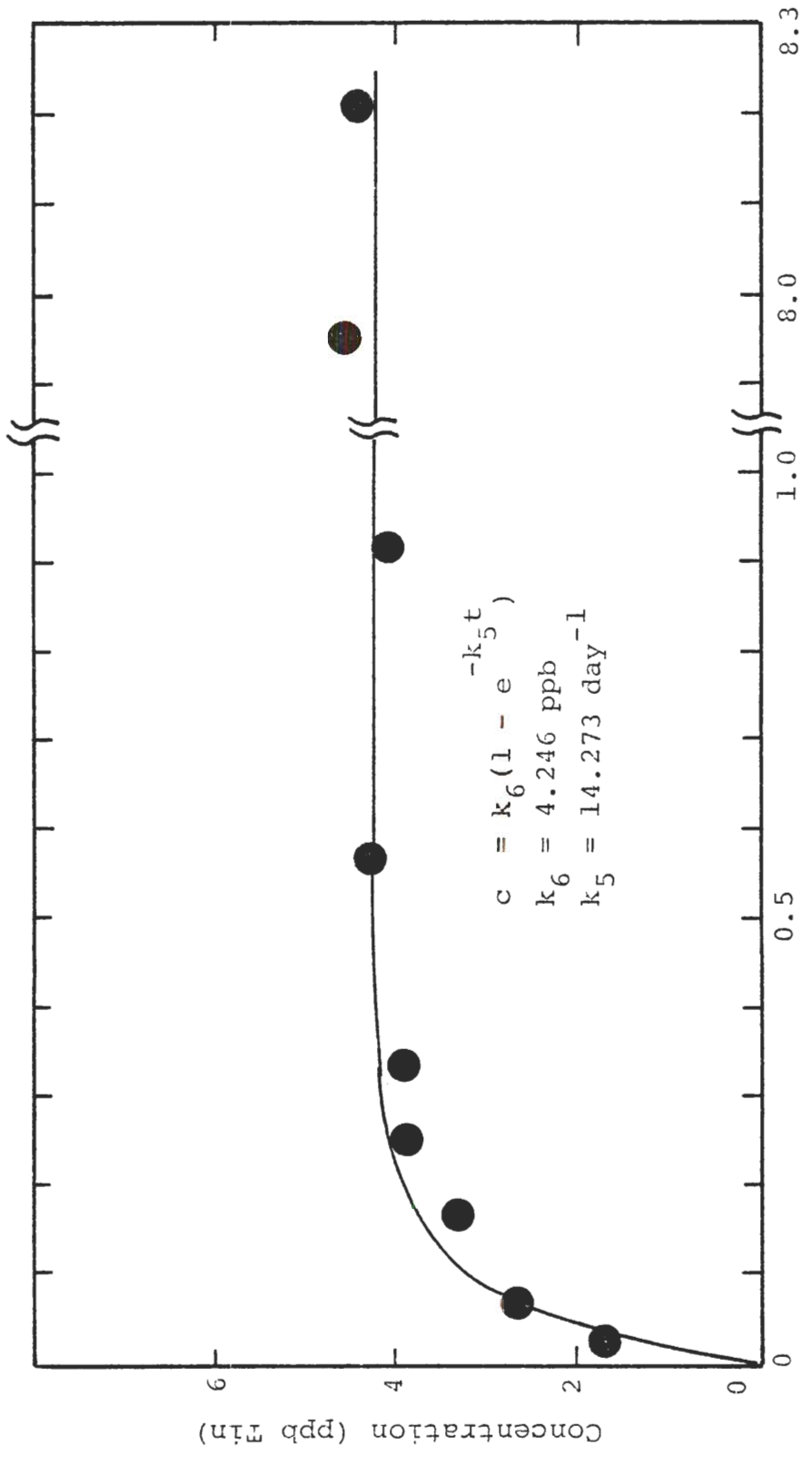


Figure 4. Experimental Results Shown on Concentration of Tin Plotted Against Time for 3.037 GPM Test.

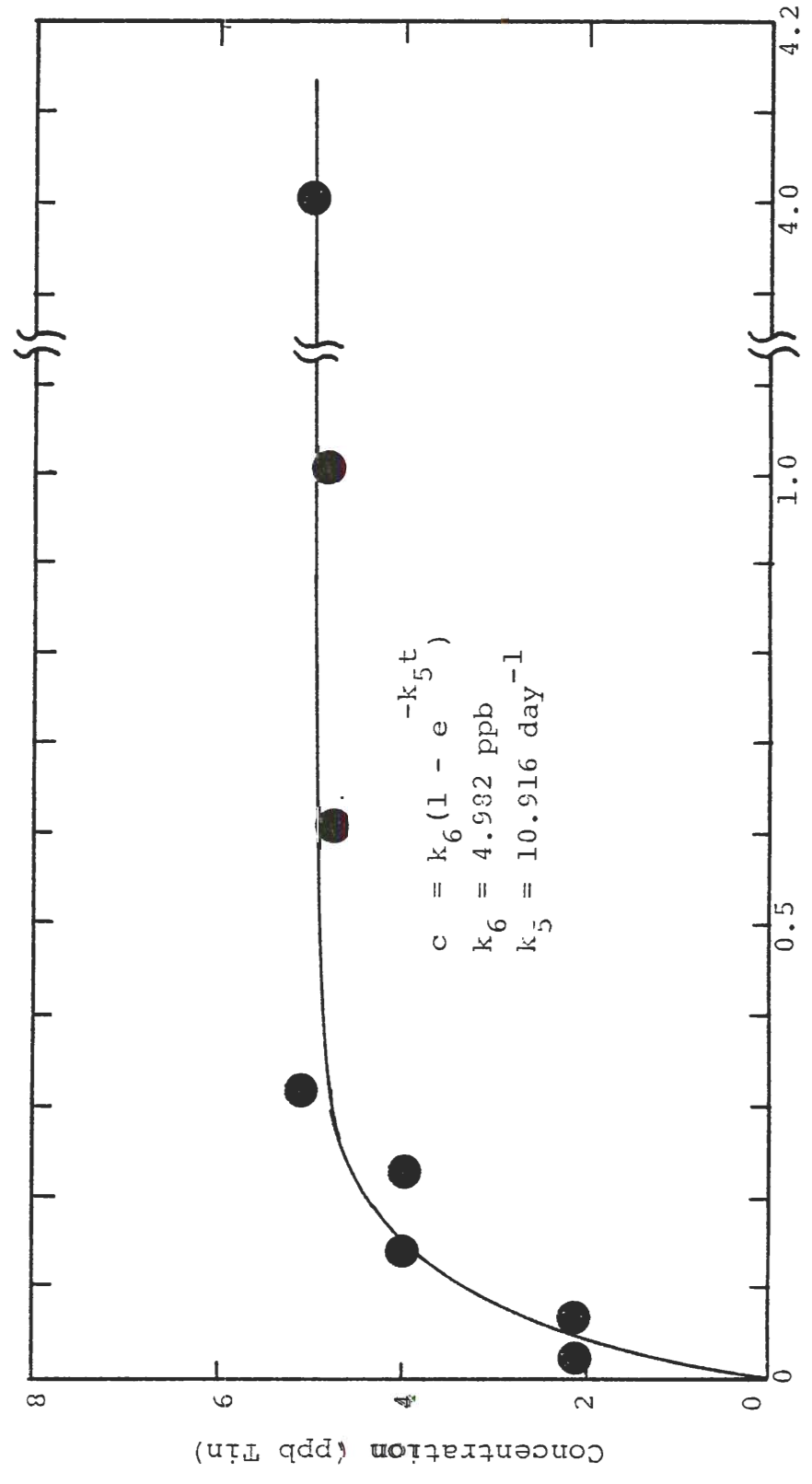


Figure 5. Experimental Results Shown on Concentration of Tin Plotted Against Time for 1.519 GPM Test.

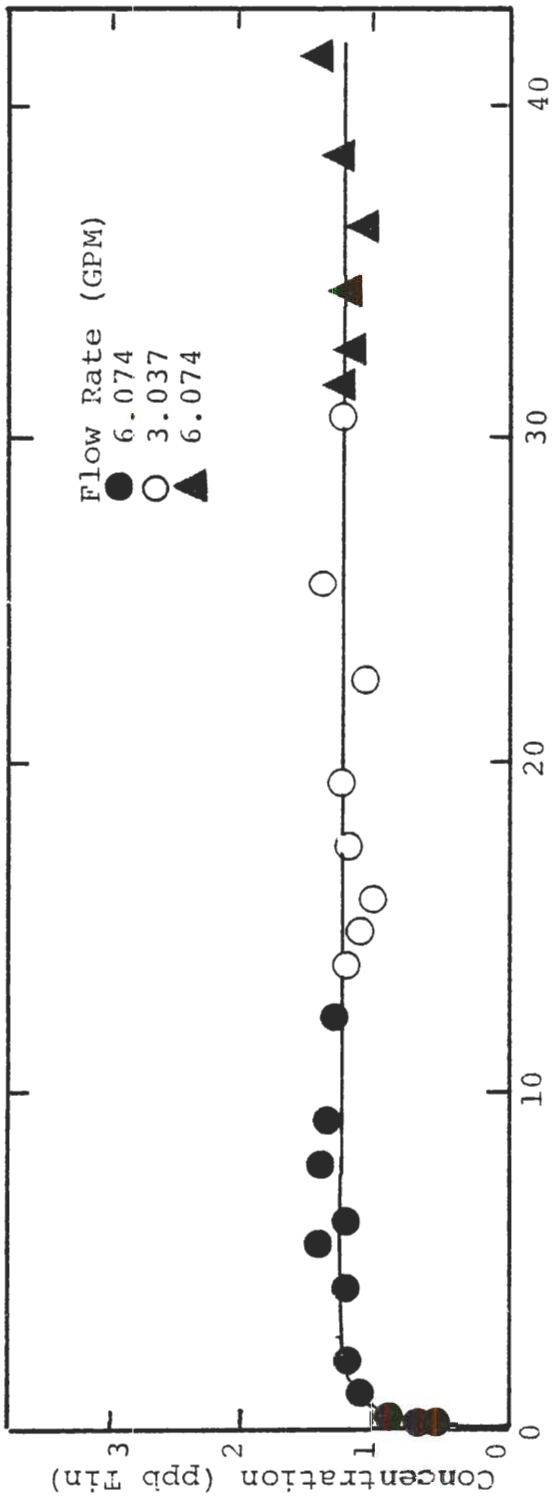


Figure 6. Experimental Results of Test No. 1 on Previously Leached Pipe.

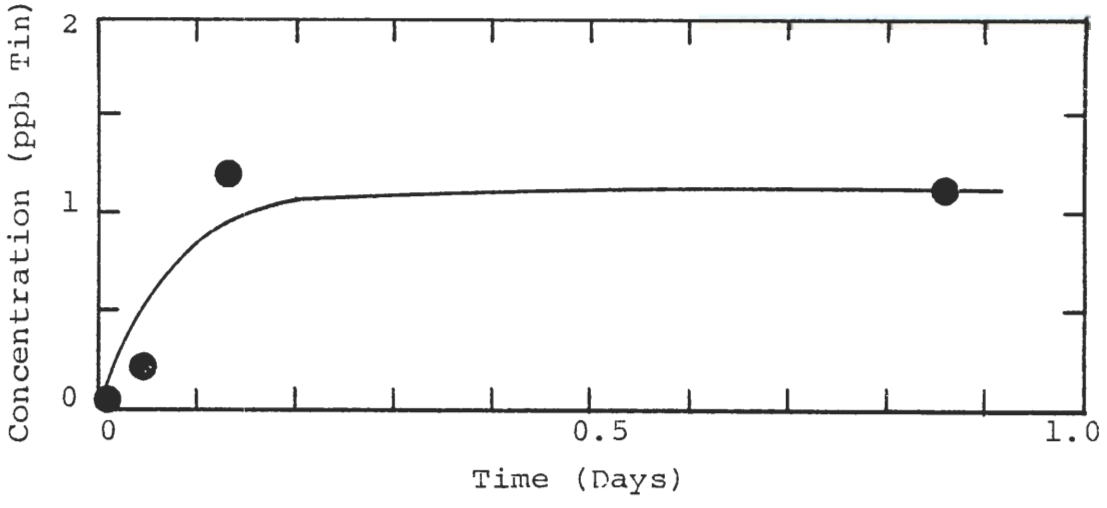


Figure 7. Experimental Results of Test No. 2 on Previously Leached Pipe.

Table 1. Results of Fitting Experimental Data With Proposed Model of Test on Unleached 3/4 in., Sch. 80 Harvel PVC 1120 Pipe.

Flow Rate (GPM)	k_6 (ppb Tin)	k_5 (day^{-1})
6.074	5.901	26.69
3.037	4.246	14.273
1.519	4.982	10.916

The 150 feet of pipe had a mass of 1.86×10^4 grams and a tin content of approximately 400 ppm. Therefore, the total tin content of the 150 feet of test pipe was 7.46 grams, and the 5.9 ppb tin represents a loss of 0.0060 percent of the total tin in the test pipe.

Since such a small fraction of tin is leached from the pipe, the low concentration of tin indicates that the organotin at or near the inner wall of the pipe was leached off, and that the migration of organotin from the bulk of the pipe due to diffusion was not significant during the test period of over 40 days.

Based on the proposed model, the relationship between the mass flux of tin from the inner wall of the pipe and time for the test system is

$$\frac{dc_s}{dt} = k_1 k_5 k_6 \, e^{-k_5 t} \qquad (16)$$

For the test system, having an initial charge of 20 gallons of water and 150 feet of test pipe with 2.71 m^2 of inner pipe

wall, the value of k_2 is $2.79 \times 10^{-5} \frac{g/m^2}{ppb}$. For the dynamic test at 6.074 GPM, the mass flux of tin was

$$\frac{dc_s}{dt} = (2.79 \times 10^{-5} \frac{g/m^2}{ppb})(26.69 \text{ day}^{-1})(5.901 \text{ ppb}) e^{-26.69t} \quad (17)$$

where t [=] days

$$\frac{dc_s}{dt} = 4.394 \times 10^{-3} \frac{g/m^2}{day} e^{-26.69t} \quad (18)$$

By assuming that the concentration of organotin compounds in the water has no effect on the mass flux of organotin compounds from the pipe wall, the concentration of tin in water which initially flows through the test pipe was calculated using the following approximation:

$$C_{initial} = - \frac{A(\frac{dc_s}{dt})}{\text{Flow Rate}} \quad (19)$$

where A is the area of the inner pipe wall. For water flowing at 6.974 GPM through 1000 feet of test pipe

$$C_{initial} = \frac{(18.1 \text{ m}^2)(4.394 \times 10^{-3} \frac{g/m^2}{day})}{3.305 \times 10^7 \text{ g/day}} \quad (20)$$

$$= 2.4 \text{ ppb Tin}$$

Therefore, a concentration of approximately 2.4 ppb tin would be attained in water emerging from 1000 feet of unleached test pipe.

In terms of dibutyltin dichloride, 2.4 ppb tin repre-

sents 6.15 ppb organotin. Therefore, the recommended maximum safety level of 20 ppb of organmetallic agents (11) might well be exceeded if the water was carried through several thousand feet of pipe.

This indicates that before new PVC pipe is used to convey drinking water, a short period (1-2 hours) of rinsing should be implemented in order to drastically reduce the concentration of organotin compounds at or near the inner wall of the PVC pipe.

The pipe used for the test unleached pipe at 6.074 GPM and the pipe used in Test No. 2 on leached pipe were the same pipe. With the assumption that the loss of tin during the rinsing between these tests was negligible, and with the assumption that the equilibrium relationship between the tin at or near the inner pipe wall and the tin in the water is first order and linear, c_{wo} and k_1 was calculated from the material balance on tin which follows.

$$c_{wo} = k_6' + k_2 + k_6'' k_2 + c_{wf} \tag{21}$$

where k_6' = equilibrium c reached in the test on unleached pipe

k_6'' = equilibrium c reached in the test on leached pipe

c_{wf} = c_w obtained at equilibrium in the test on leached pipe

Since

$$k_1 = (c/c_w) \text{ equilibrium} \tag{22}$$

then

$$k_1 = \frac{k_6'}{c_{wo} - k_6' k_2} \tag{23}$$

and

$$k_1 = \frac{k_6''}{c_{wf}} \tag{24}$$

Combining Eq. 16, 18, and 19, the relationship for c_{wf} becomes

$$\frac{k_6'}{k_6' k_2 - c_{wf}} = \frac{k_6''}{c_{wf}} \tag{25}$$

By plugging in the values of k_6', k_6'', and k_2, the value of c_{wf} was calculated to be $7.32 \times 10^{-6} g/m^2$. Therefore, the values of k_1 and c_{wo} are $1.53 \times 10^5 \frac{ppb}{g/m^2}$ and $1.96 \times 10^{-4} g/m^2$, respectively.

With the relationship

$$K_x = \left(\frac{k_2}{k_1 k_2 + 1}\right) k_5 \tag{26}$$

the value of K_x were calculated for the dynamic pipe loop tests on unleached pipe. The values of K_x, along with the Reynolds Number are given in Table 2. By assuming the relationship between K_x and Re is as follows

$$K_x = c_1 (Re)^{c_2} \tag{27}$$

the data was least squares fitted, as indicated in Figure 8. The values obtained for c_1 and c_2 were 2.22×10^{-7} $\frac{g/m^2}{ppb\text{-}day}$ and 0.62, respectively. The value of c_2 given by the Sieder and Tate Correlation is 0.8 for highly turbulent flow. Thus, considering the scatter of data as indicated in Figure 8, the value of 0.62 for c_2 is in fair agreement with the value of 0.8.

Table 2. Calculated Values of Re and K_x for Test on Unleached Pipe.

Flow Rate (GPM)	Re	K_x ($\frac{g/m^2}{ppb\text{-}day}$)
6.074	29,680	14.1×10^{-5}
3.037	14,840	7.56×10^{-5}
1.519	7,420	5.79×10^{-5}

The results of the static test on the U-shaped pipe loop are shown in Figure 9, along with the theoretical model fitted for the experimental data. The values of k_6 and k_5 are 8.212 ppb and 2.019 day^{-1}, respectively. In the static pipe loop test, the value of k_2 was 4.712×10^{-6} $\frac{g/m^2}{ppb}$. With Eq. 21, the value of K_x was calculated to be 5.53×10^{-6} $\frac{g/m^2}{ppb\text{-}m^2}$. There, K_x in the static test was less than a tenth of K_x in the 1.519 GPM dynamic test.

As in the dynamic test,

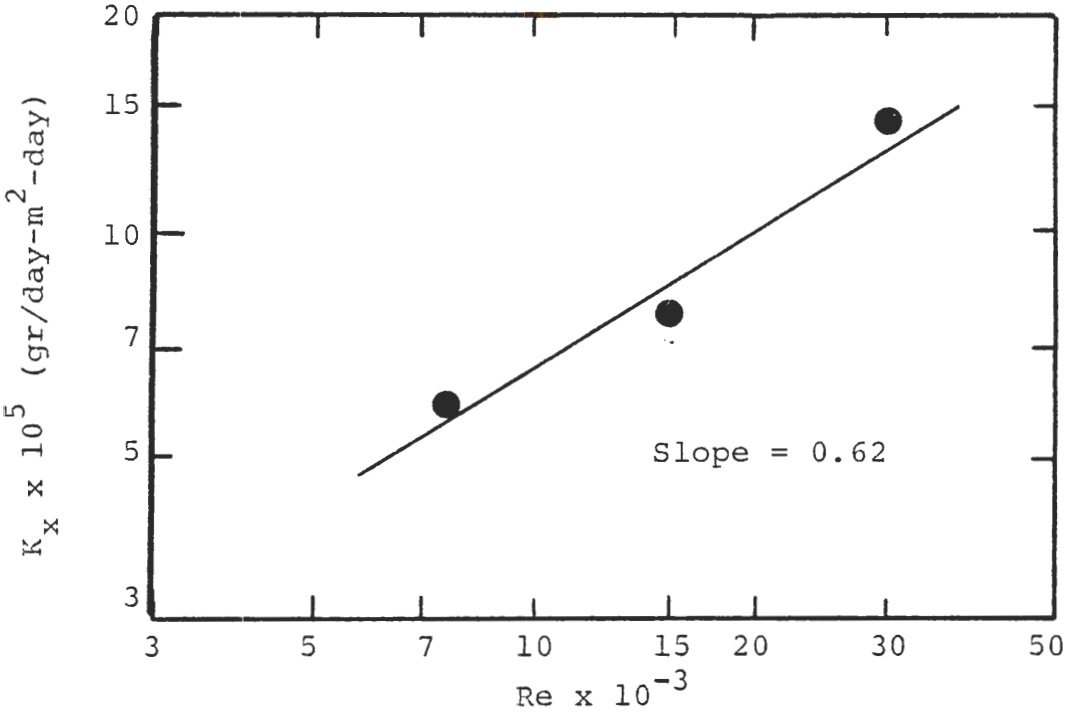


Figure 8. Log-Log Plot of K_x versus Re.

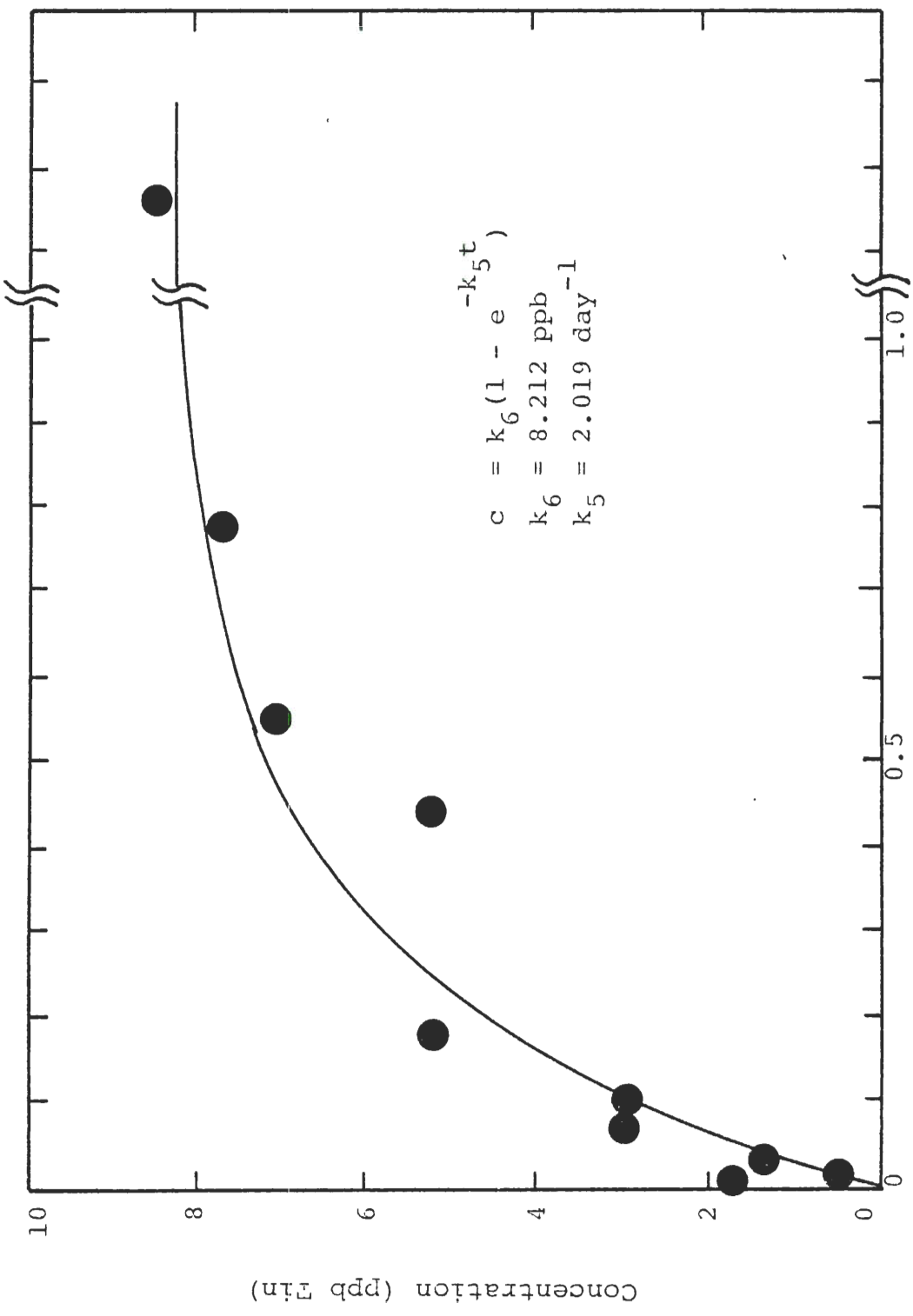


Figure 9. Experimental Results Shown on Concentration of Tin Plotted Against Time for Static Test on U-Shaped Pipe Loop.

$$k_1 = \frac{k_6}{c_{wo} - k_6 k_2} \tag{28}$$

Thus, the value of c_{wo} was calculated to be $8.21 \times 10^{-5} g/m^2$ in the static test. This is less than a half of the value of c_{wo} calculated in the 6.074 GPM dynamic test. Considering the possible sources of error, the agreement of these values is fairly good.

As stated before, the test pipe was 3/4 in., Sch. 80 Harvel PVC 1120 Pipe, a commercial product obtained from a local vendor. The uniformity of the concentration of organotin stabilizer at or near the inner wall of a 20 foot section of pipe and within walls of different sections of pipe is unknown. The randomness of the organotin surface concentration could cause some of the variation in equilibrium tin concentrations obtained in the pipe loop tests.

Another source of randomness in the testing was the rinsing of the system prior to start up of a test on unleached pipe. The author attempted to rinse the pipe in a consistent manner; however, some variation in flow rate during rinsing was not avoidable. After rinsing, the system was drained as completely as possible. A small quantity of water, however, might still have remained in the pipe. This water could have resulted in static leaching.

The samples taken during the dynamic test were assumed to have an organotin concentration equal to that of the bulk

concentration in the test water. Two principle factors affect the validity of this assumption, particularly in the initial period of the test when the rate of leaching was greatest. One factor is the manner in which the sample was taken. Since the sample was collected from the stream returning to the tank from the pipe loop, the organotin concentration of the sample could have been somewhat higher than the bulk concentration. The other factor is that the only mixing of test water in the tank resulted from recirculation. Although recirculation, particularly at the higher flow rates, results in a considerable mixing effect, the mixing in the system may not have been sufficient enough to result in a uniform organotin concentration in the tank.

Since the concentration of organotin in the test water was in the area of several parts per billion, the AA spectrophotometer was working near the limits of its sensitivity. This could result in a reduction in the accuracy of the quantitative analysis of the samples. Also, since the organotin compound in the test water has not been qualitatively determined, the use of stock solutions of dibutyltin dichloride for the calibration may have resulted in a systematic error. Solutions of different organotin compounds, having equal tin concentration, do result in somewhat different AA responses.

No discussion of sources of systematic and random errors in the dynamic pipe loop tests can be complete without

mentioning contamination. Great care was taken to avoid contamination of the test water and samples. However, since such low levels of organotin compounds were detected, any amount of tin contamination could have resulted in significant error in the quantitative analysis of organotin compounds in the test water.

Electron Microscopy Tests

From the examination of 22 samples of unleached Harvel PVC 1120 pipe by SEM, a considerable degree of variation in the microstructures on the surface was apparent. The same variety of surface features was also seen in the 22 samples of leached pipe.

The microstructures found most commonly on the inner surface include protuberances and particle-like structures. Other microstructures observed include ridges, cracks, and creater-like structures. In some samples, the protuberances appeared to be in columns which go along the length of the pipe. In other samples, ridges and particle-like structures appeared in small regions which surrounded by large areas of relatively smooth surface.

In Figures 10, 11, 12, and 13 photomicrographs of the inner surface of a SEM sample are shown. The particle-like structures and the protuberances can be seen in Figures 10 and 12, respectively. The sample, approximately ten millimeters in length was statically leached at room temperature

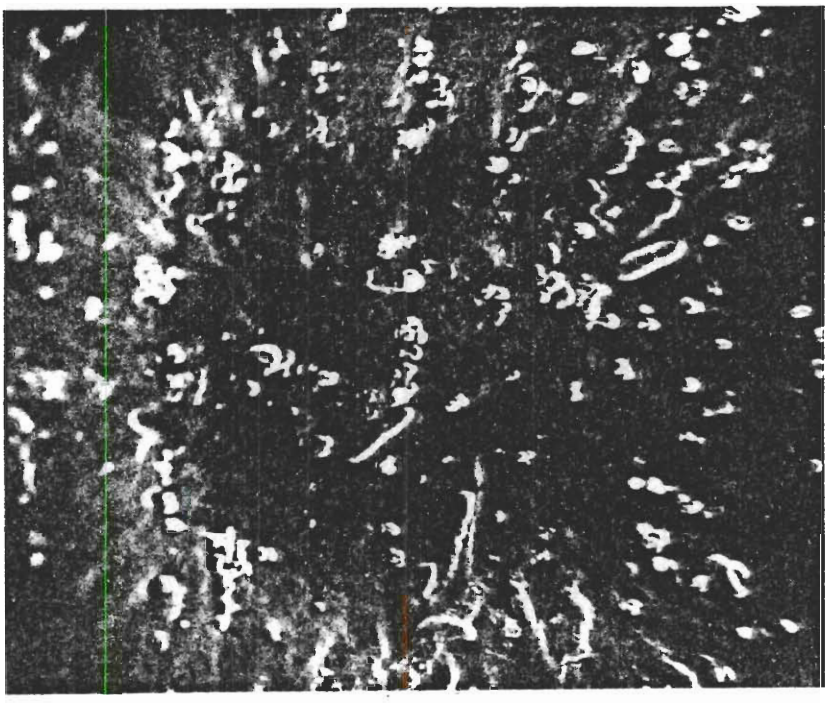


Figure 10. Leached Harvel PVC 1120 Pipe Section (Inside Surface) Magnification 5,000x.

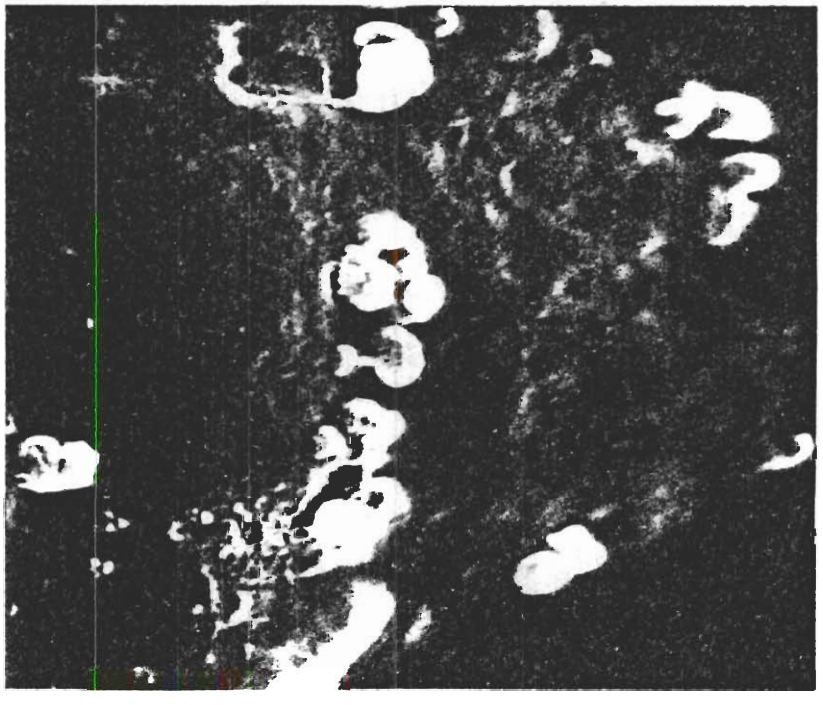


Figure 11. Leached Harvel PVC 1120 Pipe Section (Same Surface as in Figure 10) Magnification 20,000x.

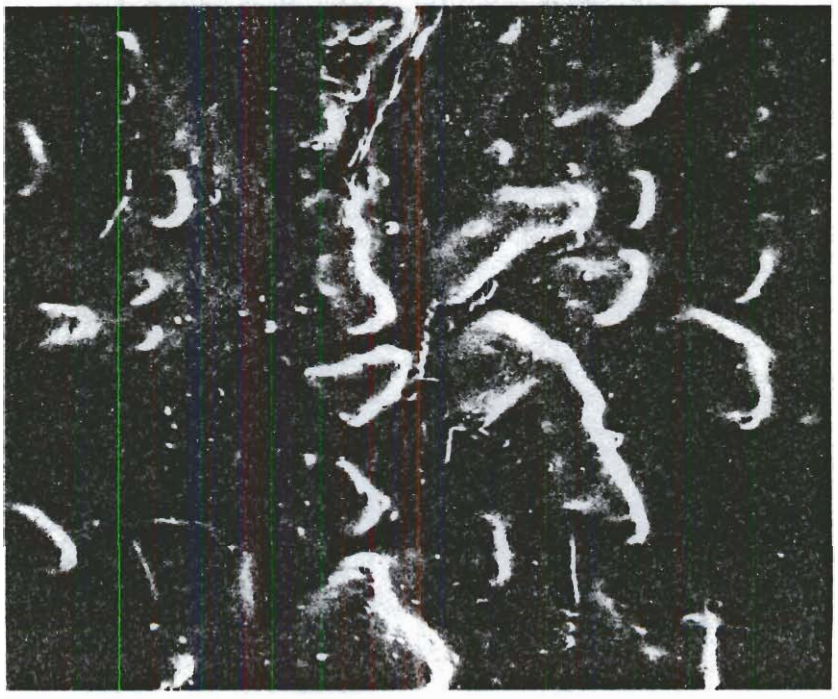


Figure 12. Precoated Harvel PVC 1120 Pipe Section (Inside Surface Adjacent to Surface in Figure 10) Magnification 5,000x.

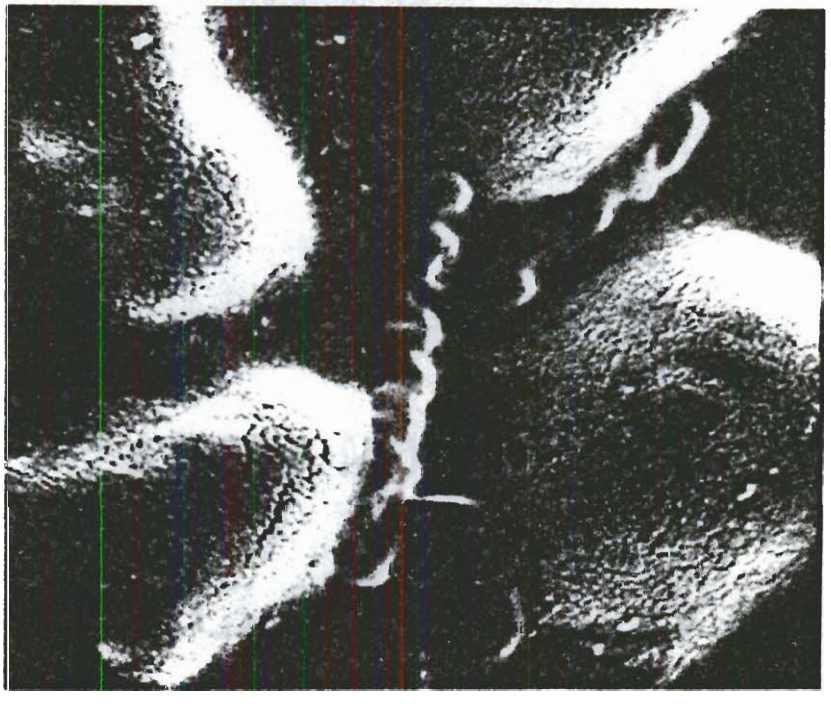


Figure 13. Precoated Harvel PVC 1120 Pipe Section (Same Surface as in Figure 12) Magnification 20,000x.

for eight days. Before the sample was placed in the high purity water, half the length of the sample was coated with gold and palladium. The purpose of the coating was to prevent changes in the underlying surface. The differences in the surface features are considerable.

The nonuniformity of the microstructures on inner surface of the Harvel PVC 1120 Pipe, as revealed by SEM, was not surprising. The PVC pipe is an extruded product, and some variation in the resin and in the processing conditions will undoubtedly occur.

Because an electrically conducting coating had to be placed on the sample prior to examination by SEM, the author was unable to examine a surface before and after treating it. To partially compensate for this, halves of some SEM samples were coated prior to leaching. In order to test the effect of the coating on the samples, some half-coated samples were stored at room temperature without leaching. After several days, the samples were entirely coated. Examination by SEM revealed that the surface features of both halves of a sample were similar in most cases.

No definite statement can be made about the effect of leaching on surface features because of the nonuniformity of the inner surface and the inability to examine an uncoated surface. In some cases, the leached surface appeared to be somewhat smoother than an adjacent precoated or unleached surface. In other cases, the opposite was true. Overall,

however, the leached samples did appear to be somewhat smoother, without as many particle-like structures. Whether or not these microstructures are rich in organotin compounds is not presently known.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The dynamic test on 3/4 in., Sch. 80 Harvel PVC 1120 pipe indicated that an equilibrium in organotin compounds was attained between the inner wall of the PVC pipe and the high-purity water recirculated through the pipe. The dynamic tests also indicated that the organotin compounds at or near the inner pipe wall were leached off by the water, and not replenished by diffusion of organotin compounds in the bulk of the wall. Based on these indications, a theoretical model having the following form was derived for the dynamic test system:

$$c = k_6 (1 - e^{-k_5 t}) \qquad (15)$$

where c = concentration of tin in test water

k_6 = model parameter whose value c attains at equilibrium

k_5 = model parameter which is a function of the mass transfer coefficient

t = time

From this model, the leaching rate is predicted to be a decaying exponential function for any PVC pipe loop.

Calculations indicate that the concentration of organotin compounds in water which initially emerges from

several thousand feet of unleached 3/4 in., Sch. 80 Harvel PVD 1120 pipe can be well over a suggested maximum safe level. The leaching rate, however, can be lowered to a safe level by simply rinsing the pipe for a period of 4 hours at a Reynolds number of 7,000 or more.

The mass transfer coefficient, K_x, for the migration of organotin compounds from the inner surface of the pipe to the flowing water is a function of Reynolds number. Based on calculated data from three tests on unleached pipe at different flow rates, K_x is proportional to the Reynolds number raised to the 0.62 power. Considering the scatter in the data, the value of 0.62 agrees favorably with the value of 0.80 reported by Sieder and Tate (17).

The examination of the inner surface of 3/4 in., Sch. 80 Harvel PVC 1120 pipe reveals the microstructures on the surface, which include protuberances and particle-like structures, are not uniform in size and distribution. Although no definite change in the surface due to leaching was found, the leached surface appeared to be somewhat smoother than the unleached surface.

In order to better assess the health hazards of the organotin stabilizer which leach from PVC pipe, a qualitative analysis of the organotin compounds leached from PVC pipe would be beneficial. Also, in order to extend the results of this study to the everyday use of PVC pipe, tests using water containing known concentrations of solutes found in

potable water should be made.

The significance of the diffusion of organotin compounds from PVC pipe should be determined through experimental studies. Also further experiemental studies should be done to determine the equilibrium isotherms for the concentrations of tin in PVC pipe-water systems.

APPENDIX A

NOMENCLATURE

A	Surface area of inner wall of pipe, [m^2]
c	Concentration of tin in test water, [ppb]
c_w	Concentration of tin at or near inner pipe wall in terms of mass per unit area, [gr/m^2]
D	Inner diameter of pipe, [m]
D_A	Molecular diffusivity, [m^2/day]
f	Friction factor
K_x	Mass transfer coefficient, [gr/day-m^2-ppb]
k_5	Model parameter which is a function of K_x, [day^{-1}]
k_6	Model parameter which is a function of c_w at time zero, [ppb]
k^+	Dimensionless mass transfer coefficient
L	Wall thickness, [m]
M	Fraction of original species which escapes from wall or pipe
N_A	Molar flux, [gr-moles/m^2-day]
Nu	Nusselt Number
R	Inner radius of pipe, [m]
Re	Reynolds Number
Sc	Schmidt Number
T	Temperature, [°K]
t	Time, [day]
u*	Shear velocity, [m/day]

APPENDIX B

MATERIALS STUDY

For the plating study, a 50 gallon hemispherical aluminum tank was partially filled with approximately five gallons of 44 ppb tin solution. Samples were withdrawn after three and five days. A plot of tin concentration versus time, Figure B1, indicated that the tin was significantly plated out.

After the aluminum tank was found to be unacceptable, a 100 gallon copper tank was considered. The plating study of copper was conducted by placing approximately 65 grams of copper turnings in a 250 ml. beaker along with 200 ml. of a 350 ppb tin standard. The amount of copper used corresponded to a surface area of about 225 cm^2. A control beaker containing only the tin standard was placed alongside the test beaker. Both beakers were covered and allowed to stand at ambient temperatures for 53 hours. The excellent agreement between the results of the quantitative analysis of the samples taken from beakers with and without copper makes it clear that no plating took place. Since copper was an acceptable material, a further examination of the tank was made. The metal allow used to solder the fittings onto the tank was analyzed to be lead and tin; thus, the copper tank also had to be rejected.

Tests similar to those on the copper turnings were also conducted on 304 stainless steel turnings. The test results indicated that 304 stainless steel was also an acceptable material.

Stability of tin solution samples stored in polyethylene and polypropylene bottles was compared with samples stored in glass bottles for a one-month period. The stored-in-glass samples deteriorated to about 50% of their original concentration. The samples stored in polyethylene and polypropylene showed no significant decreases in concentration.

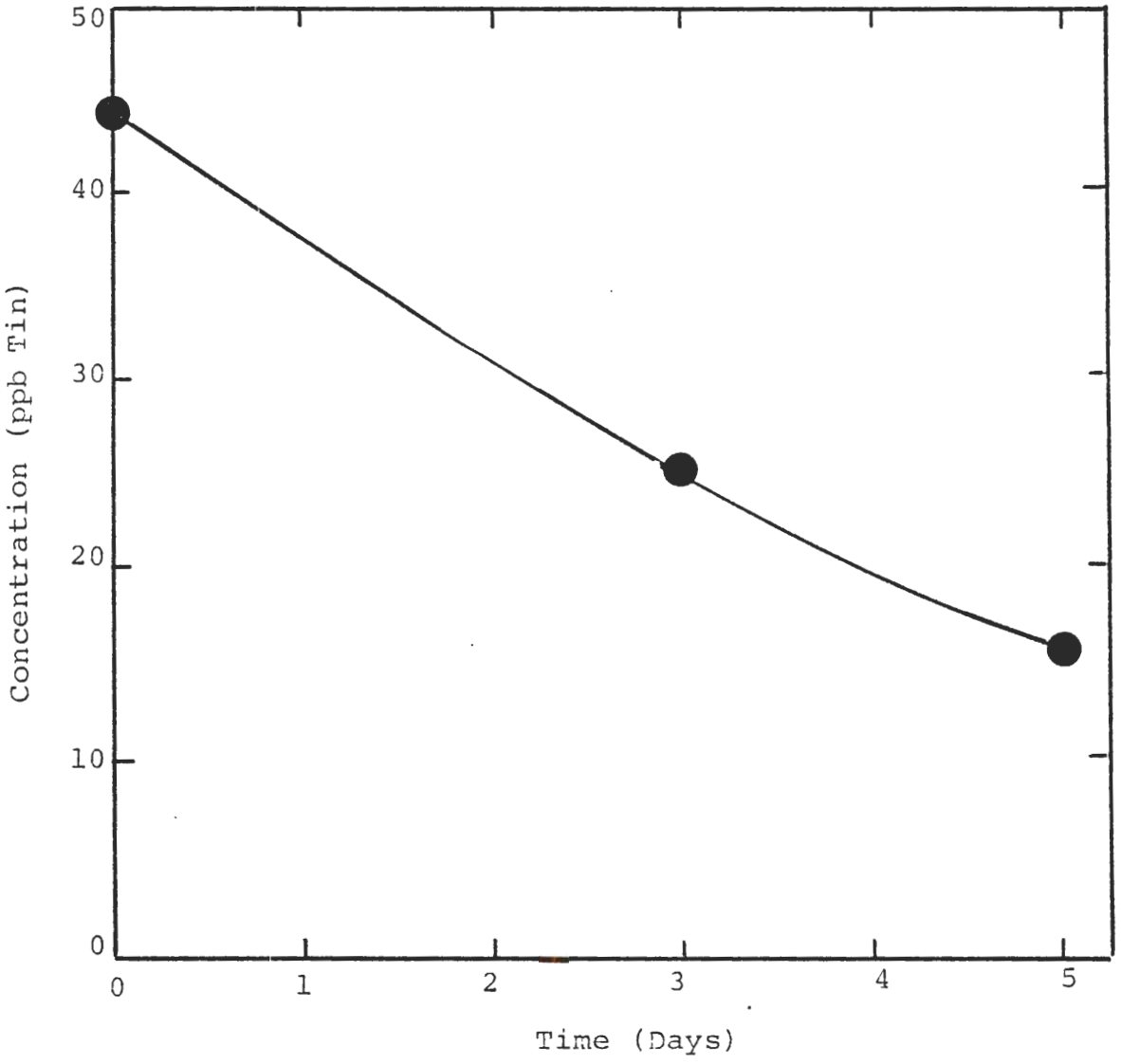


Figure B-1. Aluminum Tank Plating Results.

APPENDIX C

AA METHOD

The quantitative analysis of organotin compounds in the samples taken from the dynamic pipe loop test were run by members of the staff of the Engineering Experiment Station at Georgia Tech. This analysis was directed by Dr. Stephen Havlicek and Dr. Jack Ralls.

The analyses were run using a flameless atomic absorption (AA) method. This method has been optimized for maximum sensitivity and tested under a wide variety of operating conditions. The concentration range for which the AA method had been developed was 0.4-40 µg/l as tin or 1.0-100 µg/l as dibutyltin dichloride. The standard operating conditions were established, and the optimum instrumental parameters were as follows:

1. Tin electrodeless discharge lamp
2. Wavelength 224.6 or 286.3 nm
3. Drying conditions - 95-100°C
   a. 60-80 sec for 100 µl sample
   b. 50-55 sec for 50 µl sample
   c. 40 sec for 20 µl sample
   d. 35 sec for 10 µl sample
4. Charring conditions 500-700°C for 30 sec
5. Atomizing conditions - 2400°C for 12 sec with nitrogen

interrupt at 7 or 8 sec

6. For P-E 303 AA Spectrophotometer, slit 4 at 224.6 nm and slit 3 at 286.3 nm, a scale expansion of 10X is used for concentrations below 4 µg/l expressed as tin and 3X for concentrations from 4 µg/l to 40 µg/l. Noise suppresion with a relatively short time constant (approximately one sec) were employed.

Calibration of AA method was done by running standard samples of known concentrations of dibutyltin dichloride. The standard smaples were prepared from stock solutions of 100 µg/l dibuthyltin dichloride. Stock solutions were prepared by dissolving the appropriate amount of highly purified dibutyltin dichloride in no more than 50 ml. of high-purity methyl alcohol, adding 50 ml. of high-purity 6 normal hydrochloride acid (HCl) and diluting to 500 ml. with high-purity deionized water. Dilution of the stock solutions to be used as calibration standards at the time of analysis were made up in such a way as to maintain the 0.6 normal HCl concentrations in all solutions. At 3.9 µg/l tin a relative standard deviation of less than five percent was obtained.

The response of the AA spectrophotometer is recorded with a strip chart recorder. The typical raw data from an AA analysis is shown in Figure C-1. The peak heights are proportional to the tin content in the sample. Therefore, a 50 µl sample of 10 ppb Sn and a 100 µl sample of 5 ppb Sn will give the same peak heights. The calibration curve of the

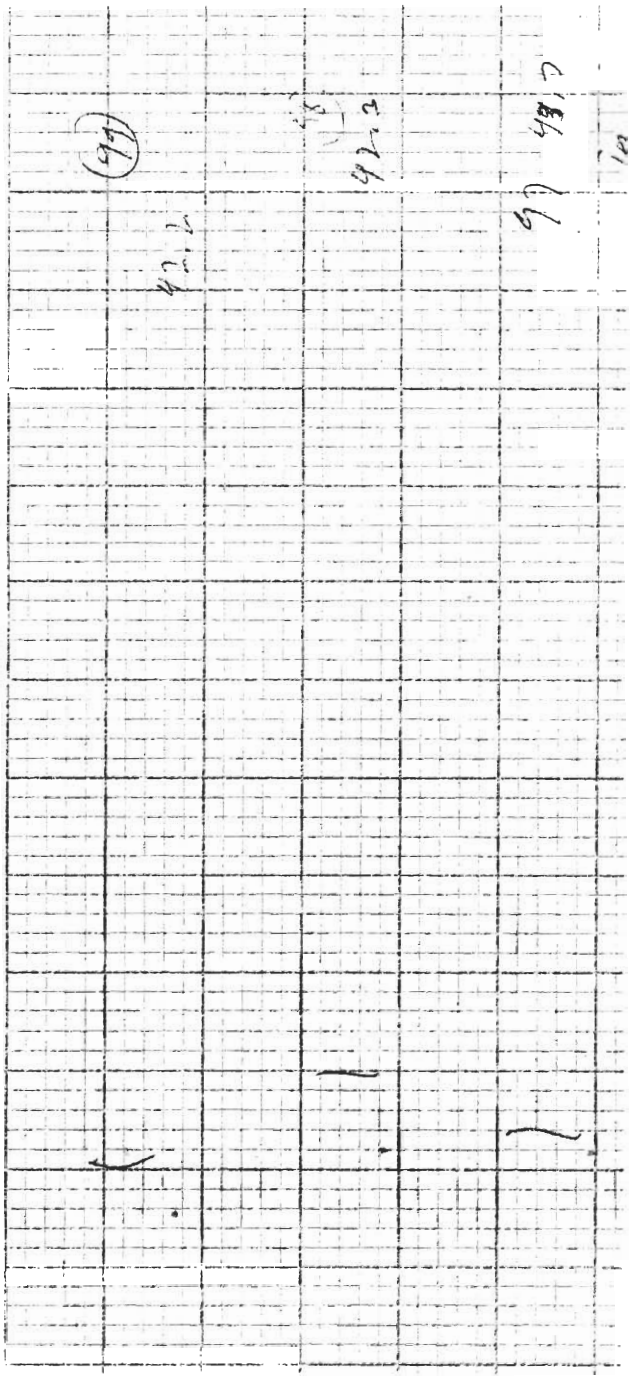


Figure C-1. Typical Raw Data From Flameless Atomic Absorption Analysis.

AA unit was made by running samples with 2, 5, and 10 nanograms of dibutyltin dichloride. The result is a linear calibration curve.

APPENDIX D

The calibration curves of the orifice plates used in the dynamic pipe loop tests are attached. Figure D-1 shows the calibration curve for orifice plate A and Figure D-2 shows the calibration curve for orifice plate B.

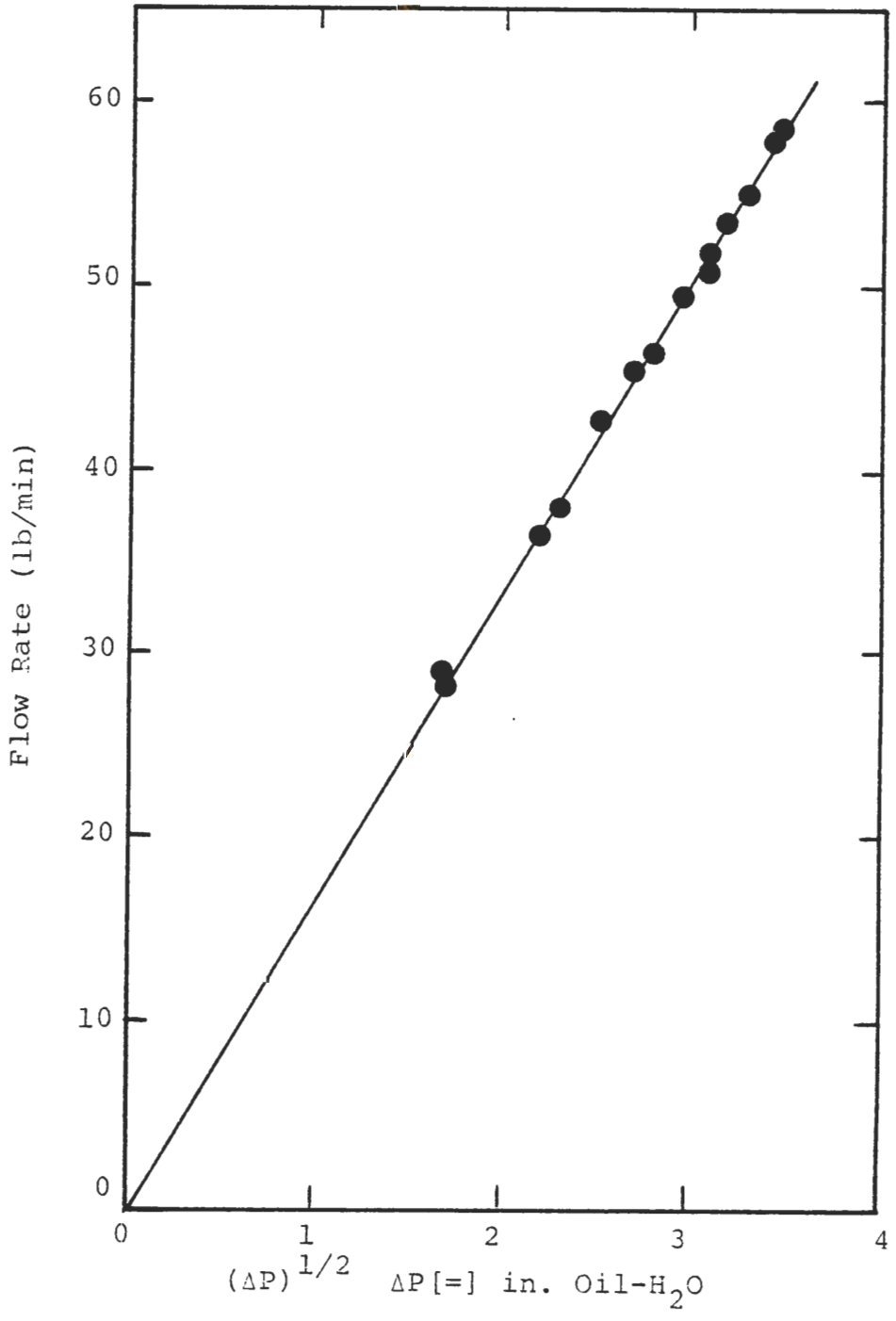


Figure D-1. Calibration of Orifice Plate A.

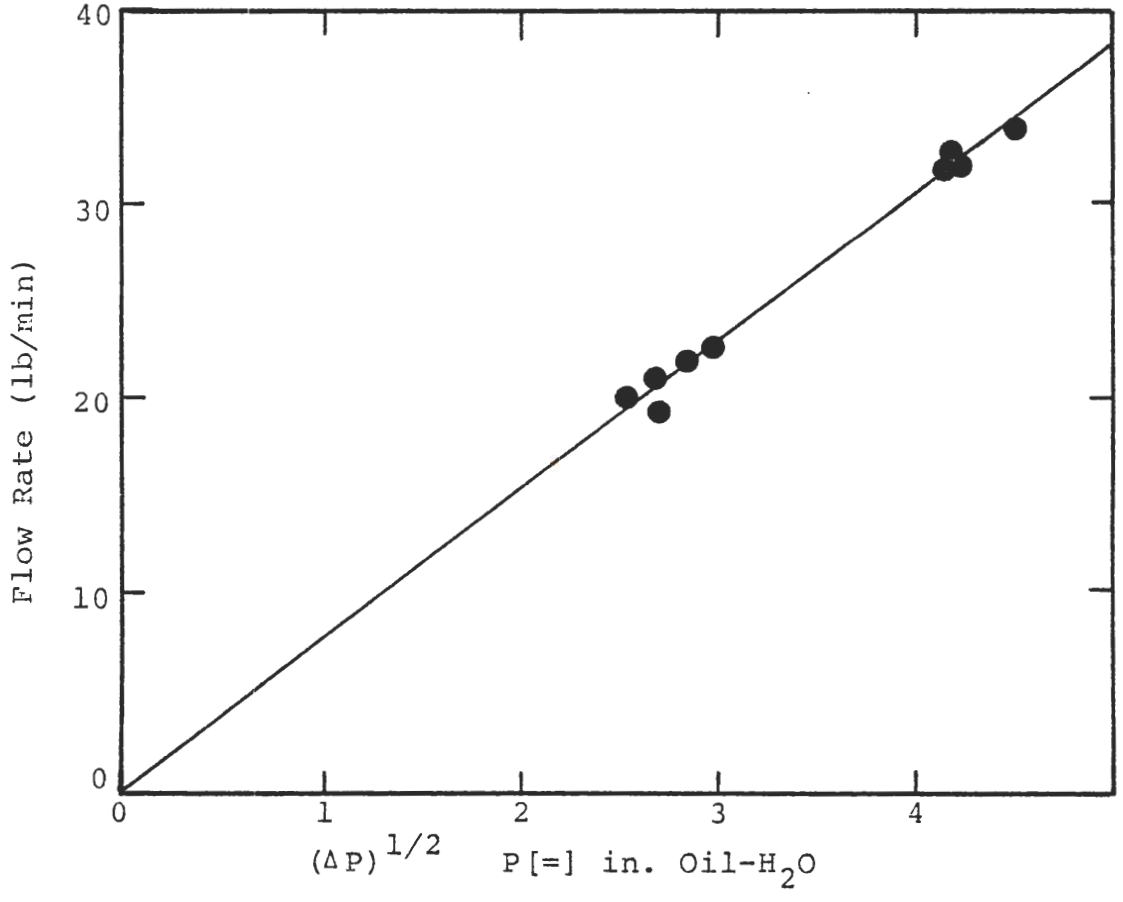


Figure D-2. Calibration of Orifice Plate B.

APPENDIX E

Table E-1. Orifice Plate and Pressure Drop Over It for Dynamic Tests of Unleached Pipe.

Flow Rate (GPM)	Orifice Plate	ΔP (in Oil-H_2O)
6.074	A	9.00
3.037	A	2.25
1.519	B	2.74

Table E-2. Pressure Drop Over Orifice Plate A for Test on Pipe Leached for 10.33 Days at 6.074 GPM.

ΔP (in Oil-H_2O)	Time of ΔP Setting (days)
9	0
2.25	12.41
9	31.24

Table E-3. Calculated Results for 6.074 GPM Test.

Time, days	Concentration, PPb Sn
.0049	1.75
.0139	2.25
.0243	3.46
.0521	3.64
.1007	4.56
.1944	5.95
.3507	5.62
.5347	6.82
1.014	7.18
1.205	4.56
1.267	5.46
1.892	6.67
2.136	5.82

Table E-4. Calculated Results for 3.037 GPM Test.

Time, days	Concentration, PPb Sn
.0210	1.67
.0625	2.62
.1667	3.29
.2500	3.81
.3333	3.90
.5625	4.29
.9170	4.05
1.146	4.07
2.146	4.25
3.167	4.81
5.083	4.38
7.958	4.57
8.208	4.46

Table E-5. Calculated Results for 1.519 GPM Test.

Time, days	Concentration, ppb Sn
.0243	2.13
.0660	2.19
.1389	3.96
.2292	3.98
.3160	5.11
.6077	4.80
1.097	4.82
2.077	5.37
2.987	5.11
4.045	4.98

Table E-6. Calculated Results for Test on Pipe Leached for 10.33 Days at 6.074 GPM (Test No. 1).

Time, days	Concentration, ppb Tin
0.021	0.54
0.056	0.65
0.278	0.92
1.028	1.10
2.07	1.17
4.17	1.21
5.61	1.39
6.24	1.21
8.10	1.39
9.32	1.35
12.40	1.30
14.11	1.20
15.00	1.09
16.00	1.03
17.61	1.18
19.51	1.24
22.61	1.06
25.60	1.38
30.74	1.23
31.65	1.26
32.74	1.15
34.45	1.19
36.52	1.04
38.63	1.25
41.50	1.42

Table E-7. Calculated Results for Test on Pipe Leached for 13.06 Days at 6.074 GPM (Test No. 2).

Time, days	Concentration, ppb Tin
.0104	0.04
.0451	0.21
.1319	1.17
.8611	1.12

Table E-8. Calculated Results for Static Test on U-Shaped Pipe Loop.

Time, days	Concentration, ppb Tin
.0104	1.71
.0278	0.48
.0764	1.38
.1493	3.00
.2153	2.93
.3646	5.18
.8889	5.19
1.115	6.99
1.563	7.56
2.344	9.07
3.984	8.36
13.11	8.36

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